



The effects of regeneration-phase CO and/or H₂ amount on the performance of a NO_x storage/reduction catalyst

Meshari AL-Harbi, William S. Epling*

Department of Chemical Engineering, University of Waterloo, Waterloo, ON N2L 3G1, Canada

ARTICLE INFO

Article history:

Received 29 May 2008

Received in revised form 25 November 2008

Accepted 11 December 2008

Available online 24 December 2008

Keywords:

NO_x reduction

NO_x storage

Vehicle emissions

ABSTRACT

The effects of regeneration-phase CO and/or H₂, and their amounts as a function of temperature on the trapping and reduction of NO_x over a model and a commercial NO_x storage/reduction catalyst have been evaluated. Overall, for both catalysts, their NO_x removal performance improved with each incremental increase in H₂ concentration. For the commercial sample, using CO at 200 °C, beyond a small amount added, was found to decrease performance. The addition of H₂ to the CO-containing mixtures resulted in improved performance at 200 °C, but the presence of the CO still resulted in decreased performance in comparison to activity when just H₂ was used. With the model sample, the presence of CO resulted in very poor performance at 200 °C, even with H₂. The data suggest that CO poisons Pt sites, including Pt-catalyzed nitrate decomposition. At 300 °C, H₂, CO, and mixtures of the two were comparable for trapping and reduction of NO_x, although with the model sample H₂ did prove consistently better. With the commercial sample, H₂ and CO were again comparable at 500 °C, but mixtures of the two led to slightly improved performance, while yet again H₂ and H₂-containing mixtures proved better than CO when testing the model sample. NH₃ formation was observed under most test conditions used. At 200 °C, NH₃ formation increased with each increase in H₂, while at 500 °C, the amount of NH₃ formed when using the mixtures was higher than that when using either H₂ or CO. This coincides with the improved performance observed with the mixtures when testing the commercial.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Increasing concerns over fuel efficiency and global warming have increased automobile manufacturer interest in diesel engine technology. However, reducing NO_x emissions from diesel engines remains a challenge. NO_x storage/reduction (NSR) technology is one solution to mitigate NO_x emissions from diesel engine exhaust. Reduction of NO_x to N₂ over NSR catalysts has been described in five sequential reaction steps [1]:

- NO oxidation,
- NO₂ or NO sorption on the catalyst surface to form nitrites and/or nitrates,
- reductant evolution,
- nitrite and nitrate decomposition thereby freeing NO_x, and
- NO_x reduction to N₂.

The first two steps occur in the lean phase, or normal diesel exhaust conditions, and the last three steps occur in a reductant-

rich phase (relative to oxygen), which is also called the regeneration phase. NSR catalysts are typically composed of alkali and alkaline metal earth components that trap NO_x in the form of nitrites and nitrates and precious metals such as Pt, Pd, and Rh for the redox reactions [1–4].

H₂, CO, and light hydrocarbons are the most common reducing agents used in NSR catalyst studies [5–12]. Several have reported that certain reductants are better at NO_x reduction than others. For example, Jozsa et al. [8] studied the influence of reductant type on the NO_x reduction efficiency of a commercial NSR catalyst using temperature-programmed reduction experiments. Their data indicated that H₂ was better than both C₃H₆ and CO for reduction of stored NO_x. Similar findings were obtained with model Pt/BaO/Al₂O₃ catalysts [9–12]. For example, during temperature-programmed experiments, the NO_x conversions were 73, 53, and 21% with H₂, CO, and C₃H₆, respectively [12]. In addition, the authors found that the ratio of NO₂/NO release was the lowest when H₂ was used in comparison to CO and C₃H₆, with almost all the NO_x being released as NO₂ when no reductant was added. The reduction efficiency of different reductants has also been examined by Fourier transform infrared (FTIR) spectroscopy on a Pt/BaO/Al₂O₃ catalyst [11]. The authors again found that H₂ was more effective than CO in reducing trapped NO_x and that when CO was used as a

* Corresponding author.

E-mail address: wepling@chemengmail.uwaterloo.ca (W.S. Epling).

reducing agent, two types of surface NCO species were readily observed. H₂O, formed from reduction of surface species with H₂ or inherent in the gas stream, can hydrolyze this NCO to another intermediate, not defined by the authors, which eventually further decomposes to N₂ and H₂O. Szailer et al. [13] found that when mixtures of CO and H₂ were used at low temperature (~147 °C), less NO_x reduction was achieved in comparison with using only H₂. They attributed the poor NO_x reduction when using the mixture to redutant competition for adsorption sites on Pt particles. With stronger CO bonding, the surface H₂ concentration would be lower in the presence of CO and if conditions favor reduction with H₂ instead of CO, the NO_x reduction rate would therefore be lowered. They also showed that NO_x conversion was higher with mixtures of H₂ and CO in comparison to just CO as the reductant under otherwise identical conditions. With only CO, NCO and CO₂ species were formed. And in the presence of H₂, the resultant H₂O hydrolyzed the NCO to form the intermediate that ultimately decomposed to N₂ and H₂O.

The formation and amounts of byproducts, such as NH₃ and N₂O, during the reduction step is also affected by reductant type. However, NH₃ formation was observed with H₂ in the regeneration phase on a Pt/BaO/Al₂O₃ catalyst [14], with a mixture of H₂ and CO on Pt-Rh/Ba/Al₂O₃ [15] and Pd/Al₂O₃ catalysts [16], and even with just CO on a Pt/BaO/Al₂O₃ catalyst [11]. Catalyst formulation does play a significant role in NH₃ formation. For example, no NH₃ is made with reduction of stored NO_x on a BaO/Al₂O₃ [17] catalyst, due to the absence of the precious metal component, which accounts for activation of H₂ in NSR catalysts. A study evaluating the influence of ceria loading on Pt/Ba/Al₂O₃ NSR performance [18] demonstrated that, under the conditions examined, as the ceria loading increased, NH₃ formation decreased. The decrease in NH₃ formation was correlated to the increase of catalyst oxygen storage capacity (OSC) with increased ceria loading; where the NH₃ that formed was consumed by reaction with the residual oxygen on the surface of the catalyst. In evaluating the effect of Ba loading on NH₃ formation over a Pt/Ba/Al₂O₃ catalyst [14], NH₃ formed only when the Ba loading was higher than 16%.

As shown above, the effect of reductant type on NSR performance has been evaluated, however, the influence of reductant concentrations and relative concentrations of the reductants in mixtures, over applicable vehicle exhaust temperature ranges has not. In this study, the effect on performance of using either H₂ or CO, and varying their concentrations in a 200–500 °C temperature range has been investigated. Furthermore, the effect of the CO:H₂ ratio in CO/H₂ mixtures on performance was evaluated. NH₃ formation was also monitored as part of this study. Redutant levels below that required to completely reduce all the trapped NO_x and account for any surface-stored oxygen were also used. This provides critical information and understanding of the effects of an incomplete regeneration due to insufficient reductant delivered, which is very possible in real application.

2. Experimental methods

Two samples in monolith form were supplied by Johnson Matthey: a model Pt/BaO/Al₂O₃ sample and a commercial sample. The model Pt/BaO/Al₂O₃ sample contains 2.0 g/in.³ Al₂O₃, and 1.45% Pt and 20% BaO relative to the Al₂O₃. The commercial sample included Pt, Rh, Ce, alkali and alkaline earth elements such as Ba, and Al₂O₃ in the formulation. Both samples were removed from monolith blocks that had cell densities of 300 cpsi. The model sample used was 0.69 in. in diameter with a length of 3 in. while the commercial sample was 0.91 in. in diameter with a length of 3 in..

Each sample was inserted into a horizontal quartz tube reactor which was placed inside a temperature-controlled furnace. The

catalyst was wrapped with 3M matting material to cover the gap between the catalyst and the wall of the reactor to ensure that no gas slipped around the sample. Two K-type thermocouples were placed at the radial center of the catalyst; one just inside the inlet face of the catalyst and one just inside the outlet face of the catalyst. Another two were placed ~1/2 in. upstream and downstream of the sample.

The gases and gas mixtures were supplied by Praxair and were metered via calibrated Bronkhorst mass flow controllers. The rich and lean gas mixtures were made in separate manifolds. A four-way, fast-acting solenoid valve was used to switch between the lean and rich mixtures. Downstream of this valve, after the dry gas mixture had been heated to >120 °C, water was introduced. Table 1 lists the gas compositions used in the cycling experiments. The wet gas mixture was then flowed through a high-capacity furnace, achieving the target test temperature prior to entering the tube furnace holding the sample. This minimized any artificial axial and radial temperature gradients during the experiments. The reactor system was also equipped with a bypass line so that the entering gases could be measured and concentrations verified.

Before each experiment, the sample temperature was ramped to 500 °C with 5% H₂O, 5% CO₂, and a balance of N₂ and then the catalyst was cleaned/conditioned with a gas mixture consisting of 5% H₂O, 5% CO₂, 1% H₂, and a balance of N₂ for 15 min. The reactor was then cooled to the target test temperature. Experiments were performed at 200, 300 and 500 °C with a space velocity, at standard conditions, of 30,000 h⁻¹. The gases exiting the reactor were maintained at >190 °C to avoid condensation and NH₃ hold-up. The gas compositions were measured using a MKS MultiGas 2030 FT-IR analyzer at approximately a 2 Hz collection rate. CO, CO₂, NO, NO₂, N₂O, NH₃, and H₂O concentrations were measured.

Water-gas-shift (WGS) experiments were performed to further understand the regeneration chemistry when CO was used as the reductant. In the WGS reaction experiments, 10–15 cycles were repeated at each temperature. A lean period of 60 s and a rich period of 30 s were used, with the lean composition containing 10% O₂, 5% CO₂, 5% H₂O and a balance of N₂ and the rich phase containing 1% CO, 5% CO₂, 5% H₂O and a balance of N₂. The WGS reaction extent values were calculated after steady-state CO and CO₂ values were reached.

Oxygen storage capacity experiments were also performed. Ten to fifteen cycles were repeated at the test temperatures. A lean period of 60 s and a rich period of 30 s were used, with the lean composition containing 10% O₂, 5% CO₂ and a balance of N₂ and the rich phase containing 1% CO, 5% CO₂ and a balance of N₂. To remove

Table 1
Details of flow conditions used in the experiments.

Flow conditions	Trapping (lean) phase		Regeneration (rich) phase
Space velocity	30,000 h ⁻¹		30,000 h ⁻¹
Concentrations			
NO	330 ppm		0
O ₂	10%		0
CO ₂	5%		5%
H ₂ O	5%		5%
H ₂	0		0–5%
CO	0		0–5%
N ₂	Balance		Balance
Temperature (°C)	Model	Commercial	Regeneration (rich) phase
200	20 s	60 s	5 s
300	30 s	150 s	5 s
500	20 s	120 s	5 s

the effect of the WGS reaction on the measured OSC, water was not used in these experiments. OSC was calculated from the amount of CO converted.

3. Results and discussion

3.1. Model Pt/BaO/Al₂O₃ sample

3.1.1. Effect of H₂ concentration

Outlet NO_x (the sum of NO + NO₂) concentrations obtained using different H₂ concentrations with an inlet temperature of 200 °C are shown in Fig. 1. For this set of experiments, the lean, or trapping, time was 20 s and the rich, or regeneration, time was 5 s. Regeneration times in practice or on the order of a few seconds, making the 5-s regeneration used here reasonable. The short trapping time, relative to real application, is due to the poorer performance of the model sample relative to a commercial catalyst, as will be shown below. The conversions, here defined as $\{100 \times (\text{NO fed} - (\text{NO} + \text{NO}_2) \text{ out}) / (\text{NO fed through an entire cycle})\}$, and amounts of NO_x trapped and released for a representative cycle during these experiments are listed in Table 2. The amount trapped was calculated based on the known amount in, and the measured amount of NO₂ and NO out during the lean phase only. NO_x release, unless explicitly stated otherwise, is the outlet NO_x amount observed during the regeneration period

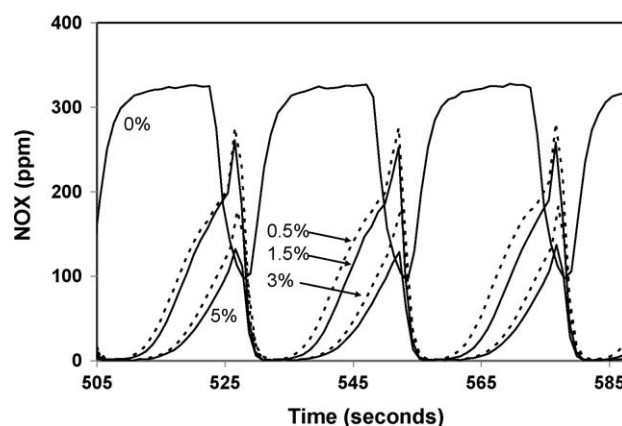


Fig. 1. NO_x outlet concentrations obtained when testing the model Pt/BaO/Al₂O₃ sample at 200 °C with 0, 0.5, 1.5, 3 and 5% H₂ in the regeneration phase.

of the cycle. Associated error was also calculated, and was <1% for trapping values and <2% for the released values. Neither N₂O nor NH₃ were included in the NO_x conversion calculation to be consistent with most literature as well as regulatory calculations. However, N₂O formation was consistently insignificant, and NH₃ formation is discussed in detail below due its mechanistic

Table 2

Calculated performance characteristics as a function of temperature, and amount of CO and/or H₂ when testing the model sample. Note: the amount of NO_x fed during one cycle at 200 °C was 43 μmol, at 300 °C was 64.5 μmol and at 500 °C was 43 μmol.

Temperature (°C)	Reductant (%)		NO _x conversion (%)	NO _x trapped (μmol)	NO _x released (μmol)	NH ₃ released (μmol)
	CO	H ₂				
200	0	0	1	2.0	3.3	1.5
	0	0.5	65	31	2.4	8
	0	1.5	70	32	1.7	17
	0	3	83	39	2.6	17
	0	5	87	40	2	20
	0.5	0	21	18	8.7	0.27
	1.5	0	19.5	17	7.9	0.18
	3	0	6	9	6	0.08
	5	0	4	7	5	0.07
	1	2	9.8	10	5.9	0.40
	1.25	1.75	9	9.8	5.8	0.55
	1.75	1.25	7.8	8.7	5.3	0.93
	2	1	6.6	8.9	6	1.2
300	0	0	1	5.5	4	0
	0	0.5	75	51	2.5	2.2
	0	1.5	85	58	1.8	33
	0	3	88	59	1.4	37
	0	5	89	59	1.2	41
	0.5	0	60	45	5.7	0.45
	1.5	0	81	56	3.5	25
	3	0	80	56	3.7	28
	5	0	79	58	6.3	31
	1	2	88	59	1.6	31
	1.25	1.75	86	58	2.0	31
	1.75	1.25	85	58	2.4	31
	2	1	85	58	2.7	30
500	0	0	2	25	24	0
	0	0.5	51	31	9	4.8
	0	1.5	55	31	7.5	6.4
	0	3	60	32	6	9.3
	0	5	62	31	4	10.6
	0.5	0	47	31	11	4.2
	1.5	0	55	31	6.5	8.6
	3	0	56	31	6	10.9
	5	0	56	30	5.5	11.6
	1	2	61	32	5.6	10.9
	1.25	1.75	59	31	5.4	14.3
	1.75	1.25	60	31	4.8	15.9
	2	1	60	30	4.2	13

significance. All reported values and plotted data were obtained once steady cycle-to-cycle performance was observed. With no reductant added, and after a steady cycle-to-cycle trend was attained, the calculated conversion was 1%, close to the expected nil conversion with no reductant at such a low temperature. With the addition of reductant, the overall NO_x conversion increased to 65, 70, 83 and 87%, with 0.5, 1.5, 3, and 5% H₂, respectively. With each increase in H₂ level, the amount of NO_x trapped increased. This is due to increased catalyst regeneration with the additional H₂. Thus, since the catalyst is being more deeply regenerated, more NO_x can be trapped in the subsequent lean phase, resulting in the increased trapping observed once steady performance was obtained. And although more NO_x was trapped in the lean phase, with additional H₂, the amounts released during the regeneration also decreased, to an extent that with 5% H₂, 95% of the NO_x trapped in the previous lean phase was reduced. This is in part due to the excess amount of H₂ introduced during the regeneration phase relative to inlet NO_x during the lean phase. The total inlet NO_x was 0.043 mmol in each cycle. With 5% H₂, 1.64 mmol of H₂ were introduced to the catalyst during the 5-s regeneration period. The reduction equation is assumed as follows; $\text{Ba}(\text{NO}_3)_2 + 5\text{H}_2 \rightarrow \text{N}_2 + \text{BaO} + 5\text{H}_2\text{O}$. Therefore for 2 mol of NO_x trapped, 5 mol of H₂ are required for reduction to N₂, or about 0.11 mmol to reduce all the entering NO_x. However, at 200 °C, 0.12 mmol of H₂ are also needed to consume surface oxygen on this sample, commonly associated with oxygen storage capacity. As a result, 1.52 mmol of H₂ remain for nitrate reduction, still in excess relative to the inlet NO_x. In fact, with only 0.5% H₂ in, or 0.164 mmol, there is almost sufficient reductant to account for both the OSC and entering NO_x. Lower H₂ concentrations do result in the observed “puff” of NO_x at the onset of the regeneration phase. This NO_x release, although there is no NO_x entering, is due to nitrate decomposition and the resulting NO_x not being reduced at adjacent or downstream precious metal sites. With less reductant, NO_x resulting from the decomposing nitrates has a greater likelihood of being released rather than reduced.

Similar experiments were carried out at 300 and 500 °C to investigate the influence of temperature on the storage and reduction of NO_x as a function of reductant level. The outlet NO_x concentration profile for a set of 30-s storage and 5-s regeneration periods at 300 °C are shown in Fig. 2. The effects of H₂ concentration on overall NO_x performance, trapping and reduction are also listed in Table 2. In the absence of reductant, and after steady cycle-to-cycle performance, the calculated conversion was 1%, again close to the expected value of 0. With the addition of 0.5 and 1.5% H₂, the NO_x conversions attained were 75 and 85%,

respectively. The calculated inlet NO_x during the 30-s lean period was 0.065 mmol and the required H₂ to reduce this amount if all was trapped and assuming nitrate formation, should be 0.162 mmol. Therefore, 0.5% H₂, or about 0.164 mmol input during 5 s, is just enough to reduce the inlet NO_x, if all was trapped. This, however, does not account for that needed to consume the OSC, which was 0.2 mmol. The entering H₂ likely first interacts with the OSC at the inlet of the sample. Once that OSC is consumed, the entering reductant can reduce nitrates at the inlet portion, where no remaining OSC exists. With the addition of 3% H₂, the NO_x conversion increased to 88% and when the H₂ concentration was increased from 3 to 5%, little overall performance change was observed as excess H₂ is now available. The NO_x conversion, trapping and release values were all similar.

The outlet NO_x concentration profiles obtained at 500 °C are shown in Fig. 3. In the absence of the reductant, the NO_x reduction efficiency was calculated to be 2%. When the H₂ concentration was increased to 0.5 and 1.5%, the overall NO_x removal performance of the catalyst increased to 51 and 55%, respectively. With further H₂ addition, the overall performance further improved, albeit marginally. It is apparent from the data in Fig. 3 that the primary differences in observed outlet NO_x concentration occur during regeneration. This is caused by the rapid decomposition of nitrates at this high temperature. Previous work has demonstrated that Ba nitrates on Ba/Al₂O₃ samples decompose between approximately 350 and 475 °C [19] and furthermore, Pt catalyzes the decomposition of nitrate species [20], at least those in close proximity to the precious metal site, suggesting that at even lower temperatures surface NO_x would be released. The entering reductant does reduce some of the NO_x being released, and as larger amounts are input, more is reduced. However, even with 5% H₂, which is more than 10 times that required to reduce the entering NO_x if all was trapped, some exits unreduced as the nitrate decomposition rate is still too rapid relative to the NO_x reduction rate with H₂.

However, not just the reduction, but also the amount of NO_x trapped at 500 °C was poor in comparison to that at 200 and 300 °C. Direct, quantitative comparison between the temperatures is not possible since different lean times were used, but trends can be evaluated qualitatively. As observed in Fig. 3, NO_x breakthrough during trapping increased sharply after just 3 s of trapping time. Although NO oxidation is also thermodynamically limited at this high test temperature, NO₂ was observed in the outlet, indicating this should not limit trapping. The overall poor performance during the lean phase at 500 °C can also be attributed to the thermal stability of nitrate and/or nitrite species [2,21–24]. Similar to adsorption/desorption rates, the formation and decomposition rates of the nitrates have different dependencies on temperature,

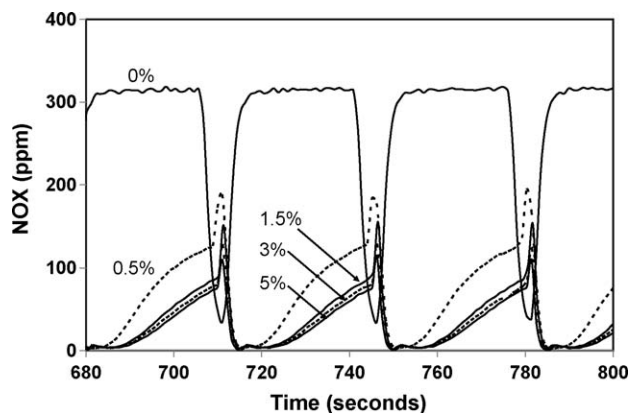


Fig. 2. NO_x outlet concentrations obtained when testing the model sample at 300 °C with 0, 0.5, 1.5, 3 and 5% H₂ in the regeneration phase.

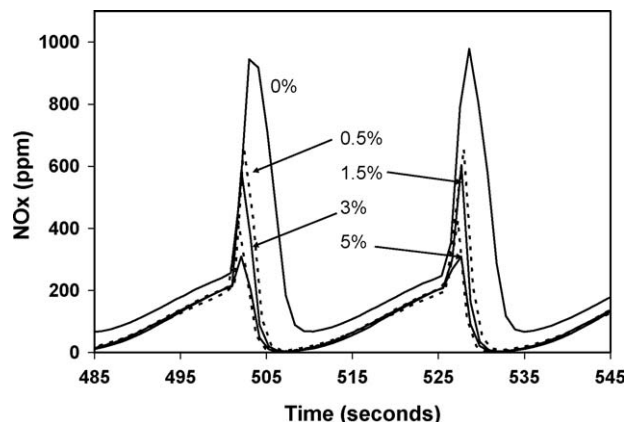


Fig. 3. NO_x outlet concentrations obtained when testing the model sample at 500 °C with 0, 0.5, 1.5, 3 and 5% H₂ in the regeneration phase.

and as the temperature is increased the decomposition rate gains significance. Therefore, although there is no inhibition to nitrate formation at such high temperatures, less of the trapping material is used due to the rapid establishment of surface nitrate/gas-phase NO_x equilibrium. At lower temperatures the decomposition rate is not as significant, shifting equilibrium between the surface and gas-phase species, thus allowing more availability of the trapping material. Therefore, at lower temperatures an equilibrium would also eventually be achieved, but with higher trapping component use than that observed at 500 °C.

Although operation at 500 °C proved worse in comparison to 200 and 300 °C, the increase in temperature from 200 to 300 °C did result in increased NO_x conversion. Again, it is difficult to quantitatively compare these data sets due to different lean times, but trends can be compared, especially at the beginning of the lean phase since regenerations were identical. First, from a kinetics perspective, NO oxidation to NO_2 increases with temperature. In general, a maximum in NO oxidation is attained between 300 and 400 °C over Pt-based catalysts [25,26], being ultimately limited by thermodynamics. As a result, the NO_2 amount will be increased at the catalyst surface resulting in higher adsorption rates, as NO_2 is more readily trapped by the alkali and alkaline earth species [27–29]. A second reason for the higher NO_x storage and reduction performance at 300 °C is the decreased thermal stability of nitrate species. When the nitrate species are too stable, NO_x may not be released upon switching from the lean to rich phase. Without release from the trapping sites, reduction and regeneration does not occur. Also, the activity for not only oxidation by precious metals is higher, but reduction rates are also higher; therefore, the rate of reduction might be faster than or as fast as NO_x release at 300 °C. Finally, another reason that has been proposed is increased surface diffusion rates with temperature [30–32]. The nitrates formed around the precious metal sites can act as a barrier toward further trapping, but if these species can diffuse to sites further from the oxidation or precious metal sites, then more trapping availability is realized. It may also be diffusion into the bulk of the Ba particles that is accelerated by increased temperature. Individually, or in parallel, these explain the increased performance between 200 and 300 °C.

3.1.2. Effect of CO concentration

Fig. 4 compares the NO_x storage and reduction performance as a function of CO concentration at 200 °C under otherwise the same conditions as those described in Fig. 1. The conversions and amounts of NO_x trapped and released for these experiments are also listed in Table 2. Increasing the CO concentration in the

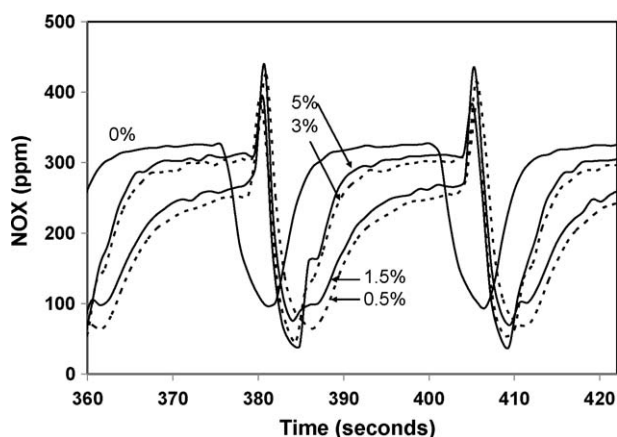


Fig. 4. NO_x outlet concentrations obtained when testing the model sample at 200 °C with 0, 0.5, 1.5, 3 and 5% H_2 CO in the regeneration phase.

regeneration period at 200 °C, beyond an addition of 0.5–1.5%, actually resulted in a decrease in the overall NSR catalyst performance. With 0.5% CO, the overall NO_x conversion was 21%, but decreased to 6 and 4% with 3 and 5% CO, respectively. With the increase from 0.5 to 5% CO, the amount trapped decreased from 18 to 7 μmol demonstrating that these drops in conversion were related to decreased NO_x trapping. CO is known to poison Pt activity at low temperature due to strong adsorption. This will directly affect the NO oxidation and NO_x reduction reaction steps when CO is present, as they are dependent on precious metal activity. Neither should have a direct impact during the lean phase though. These data suggest that the additional CO primarily impacts the amount released during regeneration. This conclusion is based on the lower amounts trapped in subsequent trapping phases when additional CO was used. Previous research has indicated that the precious metals catalyze not only NO_x reduction, but also nitrate decomposition [20], and apparently CO poisoning negatively affects this reaction process as well.

The data obtained at 300 °C with CO as the reductant are shown in Fig. 5. The cycle time was again 30 s for storage and 5 s for regeneration, as in Fig. 2. It is apparent that the increased temperature results in very different trends than those observed at 200 °C. When 0.5% CO was used during regeneration, the NO_x conversion was 60%, which increased to ~80% with 1.5–5% CO. The absence of change with the higher amounts can be explained by sufficient reductant delivery with as little as 1.5% CO, as was discussed above for the H_2 data. For example, the calculated inlet NO_x during the 30-s lean period was 0.065 mmol and the required H_2 to reduce this amount if all was trapped, assuming nitrate formation, should be 0.162 mmol, with 0.2 mmol of H_2 also needed to consume surface oxygen. Therefore, with 1.5% CO, or about 0.493 mmol input during 5 s, there is sufficient reductant to reduce the trapped NO_x .

The slight improvement in the performance of the catalyst when the H_2 concentration was increased from 1.5 to 5% was not observed when the CO concentration was increased from 1.5 to 5%. This indicates, as do the actual calculated values, that even at 300 °C, CO is not quite as effective as H_2 in regenerating the catalyst or reducing the trapped NO_x before ultimate release. This is consistent with the literature data discussed in Section 1. There are slight differences in trapping performance when either CO or H_2 was used; however, the NO_x release associated with CO was always higher, contributing to the improved NO_x conversion with H_2 . As with H_2 , there was improvement in catalyst performance with the increase in temperature to 300 °C, but with CO it was more significant than the improvement observed when using H_2 . Several reasons for the trend with increased temperature were discussed above in conjunction with the H_2 data. Most importantly though,

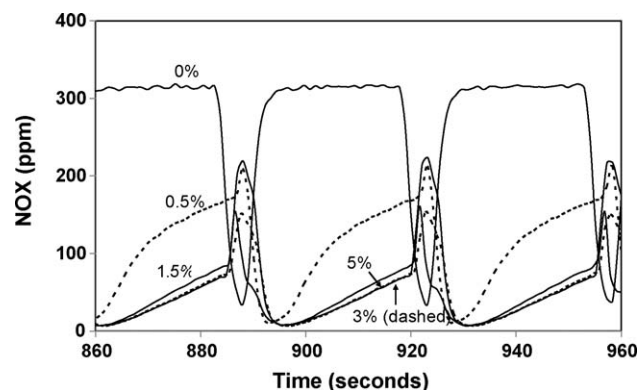


Fig. 5. NO_x outlet concentrations obtained when testing the model sample at 300 °C with 0, 0.5, 1.5, 3 and 5% CO in the regeneration phase.

when CO is used, decreased CO poisoning occurred as the temperature was increased above 200 °C, causing the significant improvement observed.

The data obtained at 500 °C when using CO as the reductant are shown in Fig. 6. The conditions are otherwise the same as those used for the data shown Fig. 3. Catalyst performance increased with CO addition to 1.5%; with 0.5% CO the NO_x conversion was 47% and with 1.5% CO it was 55%, with little change after. The increase between 0.5 and 1.5% was attained via a change in release as shown in Fig. 6 and Table 2. Beyond 1.5% CO, both trapping and release values were similar due to sufficient reductant delivery as was discussed earlier.

3.1.3. Effect of CO:H₂ ratio

Experiments were also performed with different ratios of CO/H₂, with a total reductant delivery of 3%. These data are tabulated in Table 2, but not plotted for brevity. Clearly, at 200 °C, the negative effect of the CO dominates the results. Even with 2% H₂ and 1% CO, the conversion was only 10%, well below the 83% attained with 3% H₂. Furthermore, the conversion with 0.5% H₂ was 65%, demonstrating it is not simply CO not being activated for the reactions, but also poisons the H₂ reaction pathway as well. With an increasing CO:H₂ ratio, the conversions did decrease, through small decreases in trapping, again suggesting that the CO slows the NO_x release during the regeneration phase, thus leading to poor cleaning and rapid catalyst saturation.

At 300 °C, the CO poisoning effects are significantly diminished. With 2% H₂ and 1% CO, the conversion is the same as that observed with 3% H₂. However, as the CO:H₂ ratio was increased, the conversion did decrease, approaching that obtained with just 3% CO. With the mixture, it is a combination of both decreased amounts trapped and increased amounts released that lead to the decreased conversion. At 500 °C, the conversions with all the mixtures were similar, close to 60%, the conversion attained with 3% H₂. With increasing CO:H₂, the amounts trapped did decrease, but this was balanced by a decrease in NO_x release.

3.1.4. NH₃ formation

Ammonia is a common byproduct in NSR experiments [11,33,34]. NH₃ formation has been observed when H₂ was used as a reducing agent in the regeneration period over Pt/Ba-based catalysts [14] as well as with mixtures of H₂ and CO [15], and pure CO [11]. Cumaranutunge et al. [34] have demonstrated equivalent reduction efficiency of H₂ and NH₃ in NSR catalysis at 300 °C, and facile formation of NH₃ from a feed of NO and H₂ over a Pt/Al₂O₃ catalyst. NH₃ has therefore been proposed as a hydrogen carrier or even the reductant participating in the NO_x reduction reaction. Ammonia can be formed via reaction of H₂ with NO on the catalyst,

with the H₂ added directly to the regeneration mixture or produced from the WGS reaction when CO and H₂O are both available in the regeneration mixture [35]. NO can dissociate to atomic nitrogen and oxygen over precious metals at higher temperatures [36] and subsequently, the N atom would react with dissociated H₂ to form NH₃.

At 200 °C, the amount of NH₃ observed in the outlet increased with increasing inlet H₂ levels. The amount of NH₃ produced in a catalyst channel may actually be higher, but then used to react with NO_x at downstream sites. Using CO resulted in no NH₃ observed, nor was any observed when using the mixture of CO and H₂ at 200 °C. As discussed above, CO poisoned the nitrate decomposition reaction, thus resulting in decreased trapping in subsequent lean phases. The lack of NH₃ supports this since to make NH₃, nitrates must decompose to release NO_x species to the precious metal sites for reduction.

At 300 and 500 °C, with each increase in H₂, the NH₃ increased as well, although at 500 °C, there was significantly less NH₃ observed. NH₃ was also observed with CO as the reductant, demonstrating catalyst WGS activity at 300 and 500 °C. For the CO/H₂ mixtures, relatively little change in NH₃ outlet concentrations was observed with changing CO:H₂ ratios.

3.2. Commercial sample

3.2.1. Effect of H₂ concentration

The outlet NO_x concentration profiles obtained at 200 °C using different H₂ concentrations with the commercial NSR sample are shown in Fig. 7. For this set of experiments, the lean, or trapping, time was 60 s and the rich, or regeneration, time was 5 s. The trapping time was increased due to the better performance of the commercial sample relative to the model. The conversions and amounts of NO_x trapped and released for these experiments are listed in Table 3. All reported values and plotted data were obtained once steady cycle-to-cycle performance was observed. In the absence of the reductant, and after a steady cycle-to-cycle trend was attained, the calculated conversion was 0.25%, close to the expected zero conversion with no reductant at such a low temperature. With the addition of reductant, 1.5% H₂ in the first step, the overall NO_x conversion reached 77% and with 3% H₂, the NO_x conversion increased to 85%. Smaller amounts of reductant were not used with the commercial sample due to the increased amount of OSC relative to the model sample. OSC data for the commercial sample are listed in Table 4. With further H₂ addition, little change in performance was observed; the conversion increased from 85 to 87% with the increase from 3 to 5% H₂.

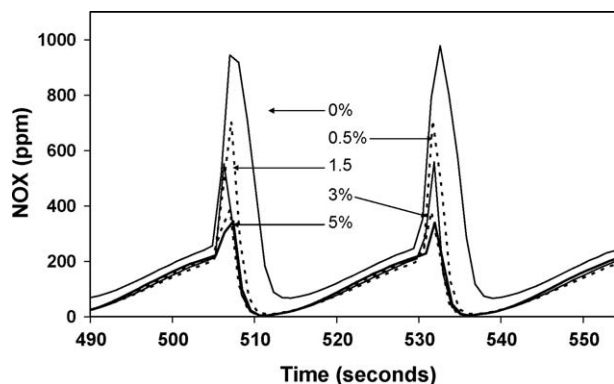


Fig. 6. NO_x outlet concentrations obtained when testing the model sample at 500 °C with 0, 0.5, 1.5, 3 and 5% CO in the regeneration phase.

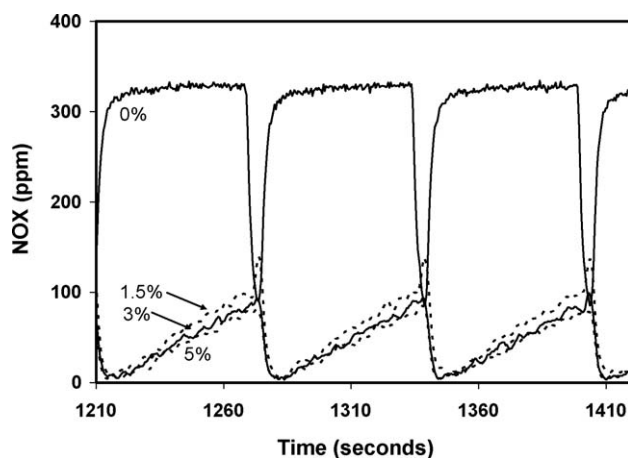


Fig. 7. NO_x outlet concentrations obtained when testing the commercial sample at 200 °C with 0, 1.5, 3 and 5% H₂ in the regeneration phase.

Table 3

Calculated performance characteristics as a function of temperature, and amount of CO and/or H₂ when testing the commercial sample. Note: the amount of NO_x fed during one cycle at 200 °C was 212 μmol, at 300 °C was 530 μmol and at 500 °C was 424 μmol.

Temperature (°C)	Reductant (%)		NO _x conversion (%)	NO _x trapped (μmol)	NO _x released (μmol)	NH ₃ released (μmol)
	CO	H ₂				
200	0	0	0.25	9	8.4	0
	0	1.5	77	169	6	52
	0	3	85	182	2	79
	0	5	87	185	2.3	101
	1.5	0	23	79	31	3.2
	3	0	15	63	31	1.6
	5	0	10	59	38	1.2
	1	2	47	117	19	35
	1.25	1.75	41	106	20	26
	1.75	1.25	36	103	28	19
	2	1	22	83	36	15
300	0	0	1	17	12	0
	0	1.5	51	272	5.5	0
	0	3	98	518	0.1	10
	0	5	98	519	0.5	64
	1.5	0	52	281	6.2	0
	3	0	96	507	2	11
	5	0	97	514	0.9	103
	1	2	98	516	1.2	17
	1.25	1.75	97	511	1.5	16
	1.75	1.25	97	513	1.5	14
	2	1	98	516	1.2	8.9
500	0	0	2.5	88	78	0
	0	1.5	32	241	105	0
	0	3	52	319	99	0.3
	0	5	67	357	77	2.4
	1.5	0	35	258	109	0
	3	0	53	327	104	0.4
	5	0	64	350	81	4.1
	1	2	54	324	97	0.9
	1.25	1.75	56	329	95	0.8
	1.75	1.25	57	333	93	0.7
	2	1	57	329	87	0.7

Just as with the model sample, with each increase in H₂ concentration in the regeneration phase, the amount of trapped NO_x increased. This is due to increased catalyst regeneration with additional H₂ and therefore increased NO_x capacity for the subsequent lean phase. Also similar to the model sample results, although more NO_x was trapped in the lean phase, with additional H₂ the amounts released during the regeneration also decreased, to an extent that with 5% H₂, 99% of the NO_x trapped in the previous lean phase was reduced. In comparing the amount of H₂ required to reduce the trapped NO_x, 0.53 mmol of H₂ would be required for reduction of all inlet NO_x, if trapped, to N₂. However, at 200 °C, 0.99 mmol of H₂ are also needed to consume the OSC on this sample, a significantly higher amount than that of the model sample, as would be expected with the presence of ceria. As a result, with 5% H₂, 1.67 mmol of H₂ remain for nitrate reduction, in excess relative to the inlet NO_x. However, 1.5% H₂ is insufficient to account for both the OSC and entering NO_x, one factor contributing to the lower efficiency observed.

Experiments were also conducted at 300 and 500 °C to again investigate the influence of temperature on the storage and

reduction of NO_x as a function of reductant level. Note, different trapping times were used to reflect more practical use of these catalysts. For example, running the trapping period at 200 °C for 150 s (as was used at 300 °C) would result in tremendous NO_x slip. Coincidentally, running a 60-s trapping period at 300 °C would result in less fuel efficiency than possible due to too frequent regeneration, and little slip and more difficult data comparison. This was also true of the model sample, but more obvious here. The basis of this work was not to compare performance at different temperatures, but to evaluate the changes in performance with changing reductant level and type, and to evaluate those trends at different temperatures. The outlet NO_x concentration profile for a set of 150-s storage and 5-s regeneration periods at 300 °C are shown in Fig. 8. The effect of H₂ concentration on overall NO_x performance, trapping and reduction is also listed in Table 3. With the addition of 1.5% H₂, the NO_x conversion attained was 51%. The calculated inlet NO_x during the 150-s lean period was 0.53 mmol and the required H₂ to reduce this amount if all was trapped, assuming nitrate formation, should be 1.33 mmol. Therefore, 1.5% H₂, or about 0.8 mmol input during 5 s, is insufficient to reduce the inlet NO_x, if all was trapped. This, furthermore, does not consider the 1.26 mmol that are needed to consume the OSC at 300 °C. Some conversion is observed though, due to the integral nature of such a catalyst system. As discussed above with the model sample data, the reductant likely interacts with the OSC first and in this case, reacts with surface oxygen at the inlet of the sample and once that is consumed, the entering reductant can reduce nitrates at the inlet portion, where no remaining OSC exists. With the addition of 3% H₂, the NO_x conversion increased to 98%. When the H₂ concentration was increased from 3 to 5%, little overall performance

Table 4

Measured oxygen storage capacities of the commercial sample at different temperatures.

Temperature (°C)	OSC (mmol)
200	0.50
300	0.63
400	0.91
500	1.1

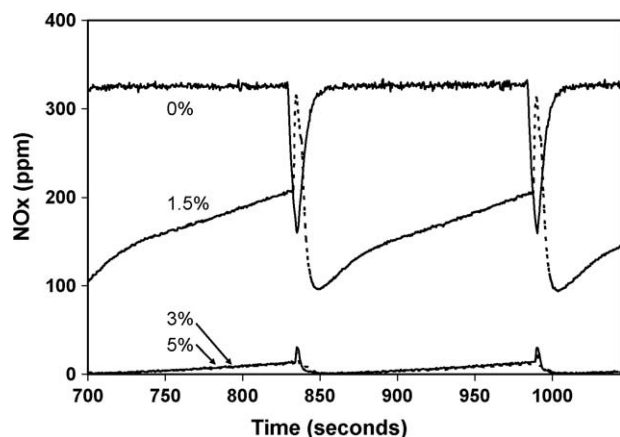


Fig. 8. NO_x outlet concentrations obtained when testing the commercial sample at 300 °C with 0, 1.5, 3 and 5% H_2 in the regeneration phase.

change was observed. The NO_x conversion, trapping and release were all similar.

The outlet NO_x concentration profiles obtained at 500 °C are shown in Fig. 9. With 1.5% H_2 , the overall performance of the catalyst was 32% and improved to 52 and 67% with 3 and 5% H_2 , respectively. This catalyst had almost $10\times$ the trapping ability compared to the model sample at 500 °C, indicating that the catalyst being tested has some high-temperature performance built into the formulation. It is apparent from the data in Fig. 9 that the primary differences, unlike with the model sample, occur during the early stages of trapping. At the end of the storage period, upon switching to the regeneration period, the difference in outlet NO_x concentrations are small, as all the available trapping material, for 500 °C trapping, has become saturated and the outlet concentration has approached the inlet value. In addition, at the beginning of the trapping phase, the NO_x level did not reach 0 ppm for the 1.5 and 3% H_2 levels. This indicates that although the rates of reaction are rapid due to the elevated catalyst temperature, the reductant amount is apparently still critical for the trapping performance. Indeed, NO_x release decreased when the H_2 concentration increased indicating that delivery rate was important, just as with the model sample.

As further discussion of this concept, when the H_2 concentration was increased from 3 to 5% at 200 and 300 °C, little difference in NO_x trapping was observed, while at 500 °C a significant difference was noted. As discussed above, stability of nitrate species and sufficient reductant delivered, coincident with lower

OSC at 200 and 300 °C lead to this result. Increasing the reductant amount from 3 to 5% at 500 °C still has a pronounced effect because of the weaker stability of nitrate species and higher OSC. For example, at 500 °C, the amount of NO_x trapped was 0.36 mmol during 5% H_2 tests. With 5% H_2 , 2.7 mmol of H_2 were introduced to the catalyst during the 5-s regeneration period, with 0.9 mmol of H_2 needed for reduction of the nitrate and 2.2 mmol needed to consume surface oxygen. Due to this high OSC value, even 5% is insufficient to reduce the trapped NO_x . This is also why a significantly higher amount of NO_x was released during regeneration in comparison to 200 and 300 °C. On top of the lack of sufficient reductant during regeneration, upon switching from the lean to rich phase, the partial pressure of oxygen drops to zero in these experiments, decreasing the stability of the nitrates further [34]. Compounding this, heat is generated via the exothermic reaction between the reductants entering and stored oxygen on the catalyst surface upon the switch from lean to rich. This generated heat raises the surface temperature, further affecting the thermal stability of the nitrate species. Release of the NO_x , or decomposition of the nitrates to an intermediate NO_x species, is ideally accompanied by reduction on adjacent noble metal sites. The rate of NO_x reduction also increases with temperature, but there is competition for the reductant between OSC consumption and the NO_x reduction reaction and therefore the actual delivery rate of the reductant to the NO_x reduction sites may not be high enough. For the experiments discussed here, the rapid decomposition of the nitrates at the higher operating temperature results in the observed, large release in Fig. 9, because enough reductant is not immediately available coincident with the large and rapid release from the surface.

3.2.2. Effect of CO concentration

The outlet NO_x concentration vs. time as a function of CO concentration at 200 °C are plotted in Fig. 10, with the experiment identical to the conditions described for Fig. 7. The conversions and amounts of NO_x trapped and released for these experiments are also listed in Table 3. Just as with the model sample, increasing the CO concentration in the regeneration period at 200 °C, beyond the first addition of 1.5%, caused a decrease in the overall NSR catalyst performance. With 1.5% CO in the regeneration phase, the overall NO_x conversion was 23%, which decreased to 15 and 10% with 3 and 5% CO, respectively. With the increase from 1.5 to 5% CO, the amount trapped decreased from 79 to 59 μmol , while the amount released increased from 31 to 38 μmol demonstrating that these drops in conversion are related to both decreased trapping and slight increases in released NO_x . As mentioned in the previous

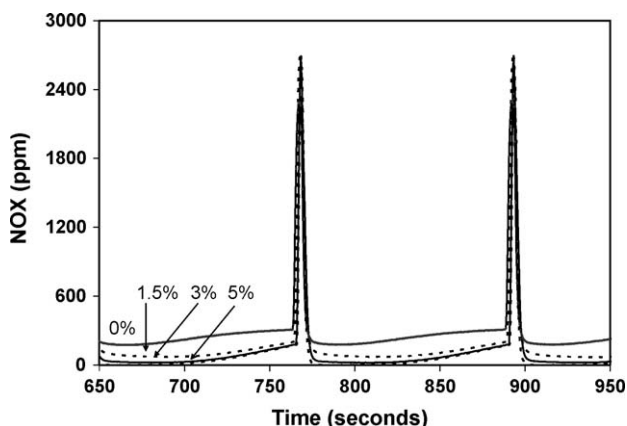


Fig. 9. NO_x outlet concentrations obtained when testing the commercial sample at 500 °C with 0, 1.5, 3 and 5% H_2 in the regeneration phase.

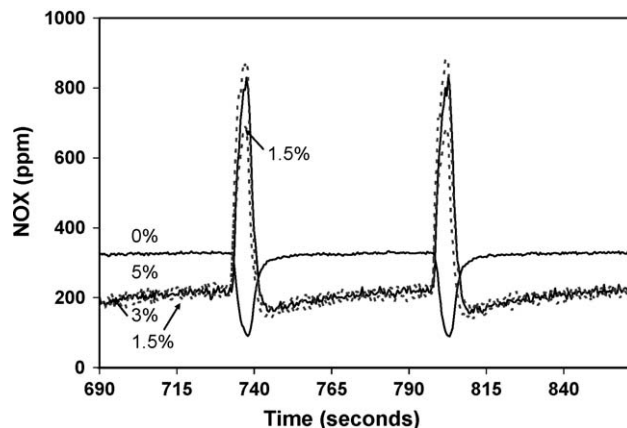


Fig. 10. NO_x outlet concentrations obtained when testing the commercial sample at 200 °C with 0, 1.5, 3 and 5% CO in the regeneration phase.

section, the probable explanation is that when CO is added at low temperature, it poisons the precious metal sites, slowing oxidation, reduction and nitrate decomposition reactions.

The little NO_x storage and reduction performance observed may have actually originated from the WGS reaction. The H₂ formed may have been the ultimate reducing agent or may have led to NH₃ formation, where NH₃ acts as a hydrogen carrier or the reductant itself [33,34]. WGS reaction experiments were performed with this sample, and at 200 °C, the maximum conversion attained was only ~10%, but enough to possibly account for some of the observed conversion. During the NO_x cycling experiments, upon switching from the lean to rich phase when CO was being used, there was a slight increase in the CO₂ outlet concentration and a simultaneous decrease in the H₂O concentration. This is also an indication that some H₂O was consumed to form H₂ during the regeneration period. Such was not observed with the model sample. But as noted, the commercial sample contains ceria, and Pt/CeO₂ catalysts are good WGS catalysts, thus possibly accounting for the WGS performance difference.

The data obtained at 300 °C with CO as the reductant are shown in Fig. 11. The cycle time was 150 s for storage and 5 s for regeneration, as in Fig. 8. Again, as with the model sample, the increase in temperature decreases the negative impact of CO poisoning. When 1.5% CO was used, the NO_x conversion was 52%, with 3% CO it was 96% and with 5% CO, 97% conversion was attained. Although the amounts released decreased, it was primarily the trapping performance that increased when the CO concentration was increased. The slight improvement in the performance of the catalyst when the CO concentration was increased from 3 to 5% was not observed when the same increase in H₂ concentration suggesting that at 300 °C, CO is not as effective as H₂ in regenerating the catalyst or reducing the trapped NO_x before ultimate release, however, this is difficult to firmly conclude with such a small change. But, this trend does match that observed with the model sample. For the commercial sample, equivalent performance was observed with 1.5% of either reductant, but this can be interpreted as the easier, or more efficient, sites being regenerated first, and not enough reductant available to regenerate more distant or more difficult to regenerate sites. Another possibility is that CO is still having to go through the WGS reaction to generate H₂ which acts as the reductant. And at higher levels of CO, the reaction is not driven to completion, thereby limiting the amount of H₂ available, so that performance with 3 and 5% reductant levels differ. As these differences are small however, it is apparent that performance using CO was overall similar to that when H₂ was used at 300 °C.

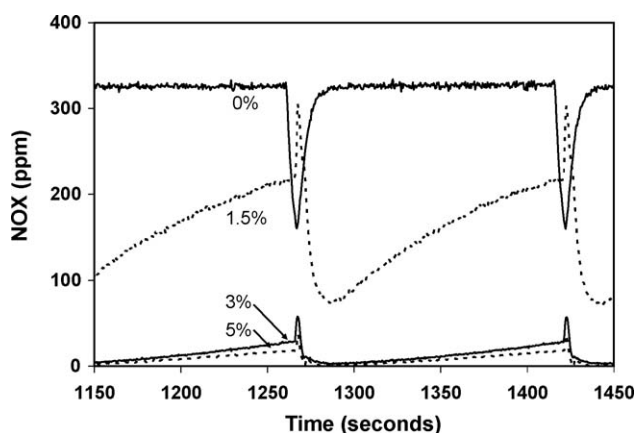


Fig. 11. NO_x outlet concentrations obtained when testing the commercial sample at 300 °C with 0, 1.5, 3 and 5% CO in the regeneration phase.

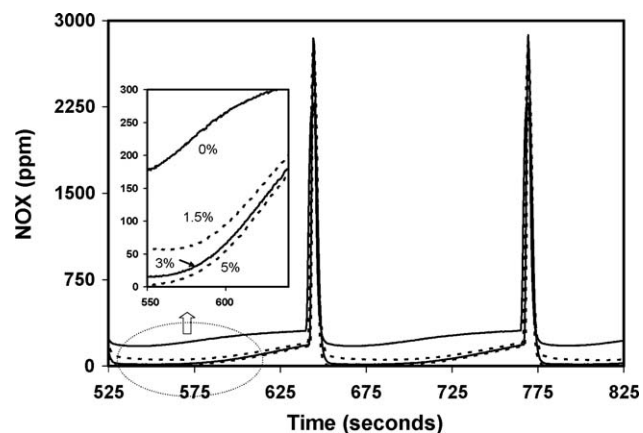


Fig. 12. NO_x outlet concentrations obtained when testing the commercial sample at 500 °C with 0, 1.5, 3 and 5% CO in the regeneration phase.

The data obtained at 500 °C when using CO as the reductant are shown in Fig. 12. Catalyst performance increased monotonically with each increase in the CO concentration. With the addition of 1.5% CO, the NO_x conversion was 35%, with 3% CO it was 53%, and with 5% it was 64%. The increase between 1.5 and 3% was attained via improved NO_x trapping, as shown in Fig. 12. There was some change in release with the increase from 1.5 to 3%, but only 5 μmol. The significant performance improvement with the change from 3 to 5% CO was not observed at the 200 and 300 °C test points, as was also noted with the model sample. This is again evidence that the NO_x release rate and OSC consumed increased faster than the reduction rate as a function of temperature.

There was a slightly higher amount of unconverted NO_x observed when CO was used instead of H₂ at 500 °C. One reason might be the increased amounts of CO₂ during regeneration, originating from the CO being oxidized. As barium carbonate is more stable than barium nitrate, the presence of CO₂ should, and has been observed to [37], lead to the decomposition of nitrates at lower temperatures than in its absence. This would in turn lead to even more rapid NO_x release. H₂O, leading to hydroxyls, could have a similar effect, but its impact has been reportedly less significant [37–39]. Another possibility is the slightly higher exothermic nature of CO oxidation compared to H₂ oxidation, leading to higher surface temperatures when using CO upon the switch from lean to rich. Due to the very sensitive stability as a function of temperature at these higher temperatures, even a small increase would lead to measurable differences in release. Lastly, any limitation in WGS activity could also result in less reduction, without much, if any, difference in subsequent trapping. Overall however, the performance of the catalyst was primarily affected by the reductant concentrations rather than type of the reductant at 500 °C.

3.2.3. Effect of CO:H₂ ratio

The performance of the commercial catalyst was also evaluated using a mixture of 3% CO and H₂. Like the experiments performed with either 3% CO or H₂, at 200 °C the lean phase was 60 s and the regeneration phase was 5 s. The calculated NO_x trapped, released and converted are listed in Table 3. It is clear that H₂ was better at 200 °C; however, it is also apparent that the CO poisoning effect was still significant. For example, with 1.5% H₂ and no CO, see Fig. 7, 77% NO_x conversion was attained. However, with 1.75% H₂ and 1.25% CO, twice the total reductant amount, and at least more H₂ than was available with just 1.5% H₂, only 41% was attained. This effect was also observed with the model sample. Overall, as the amount of H₂ in the regeneration phase was increased, the conversion did increase, but not in proportion to the amount being added due to CO poisoning. This improvement occurred via both

increased trapping during the lean phase and decreased release during regeneration. The addition of the H_2 to the CO-containing mixtures resulted in improved performance, but when CO was completely removed, a large jump in trapping performance was observed. As mentioned previously, the addition of CO poisons the precious metal sites to not just reduction of released NO_x , but also toward the catalyzed decomposition of the nitrates leading to released NO_x , further supporting the mechanism that includes reductant and the precious metal both inducing decomposition of the nitrate species [12]. Some trapped NO_x was released (for this argument, released means NO_x observed as unreduced and in the outlet, as well as that released and reduced) when only CO was used, or even when CO was present, but it is less than when H_2 was included, as is demonstrated by improved trapping in subsequent lean phases when H_2 was added.

Data obtained at 300 °C are listed in Table 3. The cycling experiment again consisted of a 150-s storage phase and a 5-s regeneration phase. The increase in operating temperature from 200 to 300 °C resulted in higher NO_x removal efficiency with the CO/ H_2 mixtures as well. The reasons for such improvement are the same as those discussed above, i.e. reduced CO poisoning. With each incremental addition of H_2 , improvement in trapping performance was still observed. However, the maximum difference in the overall NO_x conversion, and trapping, among all the reductant mixtures was only in a range of 1–2%. Both reductants are similar in efficiency, with the differences observed real, but quantitatively not very significant under the conditions of this test. Longer lean phase times may have resulted in different conclusions. The differences in trapping are still due to better regeneration of the catalyst by the H_2 reductant in a prior regeneration phase. The amount of NO_x released during the regeneration did not follow a clear trend, although it is obvious that with H_2 less was released than in the case where just CO was the reductant source.

The data obtained at 500 °C are also listed in Table 3. As was discussed previously, no significant differences were observed in the overall performance of the catalyst when using H_2 or CO in the regeneration period at 500 °C. The NO_x conversion when 3% H_2 was used was 52% while 53% conversion was achieved with 3% CO. However, when mixtures of the two reductants were used, the performance was slightly better. For example, with 1.25% H_2 and 1.75% CO, the NO_x conversion was 56%, and 57% with 1.75% H_2 and 1.25% CO. In addition, the NO_x release associated with using the mixtures of the two reductants was slightly lower than using either H_2 or CO separately. Although not definite, there are a couple of possibilities that could explain this observation. First, CO oxidation is more exothermic than H_2 oxidation whereas the activation of H_2 on precious metals is much easier than CO. The heat generated from the more exothermic CO oxidation reaction via its interaction with OSC might result in more nitrate decomposition and NO_x release, and coupled with the presence of H_2 resulted in better regeneration. Another possible reason for the improved performance relates to the formation and reduction ability of NH_3 , which will be discussed in further detail below. Briefly, however, slightly higher concentrations of NH_3 were observed in the outlet when using the CO and H_2 mixtures at 300 and 500 °C and NH_3 has been proposed as the reductant or at least as a H_2 carrier during regeneration.

3.2.4. NH_3 formation

In comparing the data at the different test temperatures listed in Table 3, it is apparent that NH_3 in the outlet increased as the temperature was decreased. At 200 °C, the NO_x -to- NH_3 reduction mechanism is rapid, relative to the reduction reaction that results in N_2 . The NO_x -to- N_2 reduction mechanistic path's rate increases with temperature until it is more comparable to the NH_3 formation mechanism and/or surpasses it. This can be due to

the reaction kinetics as a function of temperature or concentration of reactant species. The latter is likely since as the temperature is further increased, the weak stability of NO_x species causes the release of unconverted NO_x to increase, resulting in significant competition for reductant between OSC consumption and NO_x reduction to N_2 or NH_3 .

As an example of the NH_3 release profiles, the NH_3 outlet concentration data obtained from the 300 °C experiments with CO as the reductant are shown in Fig. 13. NH_3 formation at 200 and 300 °C, when H_2 was used as the reductant source, is proportional to H_2 concentration in the regeneration mixture; as the H_2 concentration increased, the NH_3 in the exhaust increased. Similarly, when CO was used at 300 °C, NH_3 in the outlet increased with increasing CO concentration from 3 to 5%. This NH_3 must originate from H_2 generated via the WGS reaction. At 200 °C however, the little NH_3 formation that was observed decreased as the CO concentration increased, as listed in Table 3. This is again attributed to the negative impact of CO poisoning on the precious metals at 200 °C. Little or no NH_3 was observed during the tests at 500 °C. However, the small amounts that did form changed proportionally to the inlet reductant concentrations; as the reductant concentrations increased, the NH_3 outlet concentration increased.

At 300 °C, NH_3 was not observed with 1.5% CO or H_2 . This is due to insufficient reductant, relative to trapped NO_x , delivered during regeneration. This does not indicate NH_3 is not formed along the catalyst, but that any NH_3 that is formed is used downstream in nitrate or released NO_x reduction. NSR catalysts operate as integral devices and spatial resolution of the chemistry along the axial length of channel is evolving. However, there are several publications that suggest NH_3 formation is constantly occurring, but the NH_3 formed can easily react with downstream nitrates of surface NO_x species to form product N_2 [33,34,39].

As listed in Table 3, at 300 °C using H_2 surprisingly led to lower levels of NH_3 in the outlet gas composition in comparison to the amount evolved when using the mixtures. This coincides with the slightly higher conversion observed with the mixtures as well. It is likely that this is due to a combination of effects. It is apparent that CO hinders NO_x release from the surface at 200 °C, and this effect may be reduced at 300 °C, but still present. H_2 , as noted, induces release. With just H_2 , NO_x release readily occurs and the local H_2 : NO_x ratio determines the amount of NH_3 made. When CO is added with the H_2 , the CO slows the release of NO_x , or decomposition of the surface NO_x species, such that the local H_2 : NO_x ratio could be higher than with just H_2 , leading to more NH_3 evolved. With just CO, the local amount of H_2 generated from the WGS reaction relative to the surface NO_x species determines the amount of NH_3 made, and although the CO would still slow NO_x

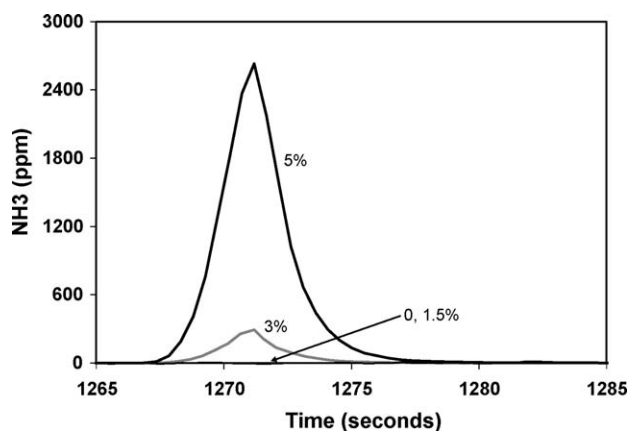


Fig. 13. NH_3 outlet concentration data obtained when testing the commercial sample at 300 °C with 0, 1.5, 3 and 5% CO in the regeneration phase.

release, the extent of the WGS reaction is only 62% at the catalyst outlet at 300 °C, with of course less at the inlet. Therefore, it is possible that with the mixtures, the CO slowed NO_x release or nitrate decomposition, and combined with the presence of H₂, resulted in more NH₃ formed. A similar argument can be made for the 500 °C operating condition, where slightly more NH₃ was also made when using the mixtures. Here, however, the extra NH₃ made down the axial length of catalyst could also result in the slight improvement in NO_x conversion observed, as shown in Table 3 and discussed above.

4. Conclusions

In this study, the performance of two samples, a model Pt/BaO/Al₂O₃ sample and a commercial NSR sample, were evaluated as a function of reductant type, reductant concentration, and temperature. Overall, for both catalysts evaluated, NO_x reduction performance improved with each increase in regeneration-phase H₂ concentration. With CO, the same was true, except at 200 °C where increasing the CO concentration, beyond 0.5–1.5%, resulted in decreased catalyst performance, which was attributed to CO poisoning of precious metal sites, thereby inhibiting not only NO oxidation and reduction reactions, but also inhibiting nitrate decomposition. With mixtures of CO and H₂ at 200 °C, the CO poisoning effect outweighed the positive effect of H₂. At 300 °C, with the commercial sample, the calculated conversions using either reductant or the mixtures were comparable, but H₂ resulted in slightly improved performance. At 500 °C, overall performance was again comparable between H₂ and CO, but best with the mixtures of reductants, rather than with just H₂, which was related to NH₃ formation. For the model sample, H₂ consistently proved the better reductant, even at 500 °C. NH₃ in the outlet was observed at all temperatures, but increased with decreasing temperature. At 200 °C, the amount formed was proportional to the amount of H₂ in the inlet, while at 500 °C, mixtures of CO and H₂ resulted in more NH₃ observed than with just H₂, although the amount of total reductant was maintained.

Acknowledgements

The authors would like to thank Natural Sciences and Engineering Research Council of Canada Discovery Grant Program and Kuwait University for financial support and Johnson Matthey for the samples provided.

References

- [1] W.S. Epling, L.E. Campbell, A. Yezerets, N.W. Currier, J.E. Parks, *Catalysis Reviews* 46 (2004) 163.
- [2] E. Fridell, M. Skoglundh, B. Westerberg, S. Johansson, G. Smedler, *Journal of Catalysis* 183 (1999) 196.
- [3] N. Takahashi, H. Shinjoh, T. Iijima, T. Suzuki, K. Yamazaki, K. Yokota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, T. Tanaka, S. Tateishi, K. Hasahara, *Catalysis Today* 27 (1996) 63.
- [4] N.W. Cant, M.J. Patterson, *Catalysis Today* 73 (2002) 271.
- [5] A. Ueda, T. Nakao, M. Azuma, T. Kobayashi, *Catalysis Today* 45 (1998) 135.
- [6] N. Takashini, H. Shinjoh, T. Iijima, T. Suzuki, K. Yokota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, T. Tanaka, S. Tateishi, K. Kasahara, *Catalysis Today* 27 (1996) 23.
- [7] M. Konsolakis, I.V. Yentekakis, *Applied Catalysis B: Environmental* 29 (2001) 103.
- [8] P. Jozsa, E. Jobson, M. Larsson, *Topics in Catalysis* 30–31 (2004) 177.
- [9] D. James, E. Fourré, M. Ishii, M. Bowker, *Applied Catalysis B: Environmental* 45 (2003) 147.
- [10] S. Poulston, R.R. Rajaram, *Catalysis Today* 81 (2003) 603.
- [11] T. Lesage, C. Verrier, P. Bazin, J. Saussey, M. Daturi, *Physical Chemistry Chemical Physics* 5 (2003) 4435.
- [12] Z. Liu, J.A. Anderson, *Journal of Catalysis* 224 (2004) 18.
- [13] T. Szailer, J.H. Kwak, D.H. Kim, J.C. Hanson, C.H.F. Peden, J. Szanyi, *Journal of Catalysis* 239 (2006) 51.
- [14] L. Castoldi, I. Nova, L. Lietti, P. Forzatti, *Catalysis Today* 96 (2004) 43.
- [15] T. Lesage, C. Verrier, P. Bazin, J. Saussey, S. Malo, C. Hedouin, G. Blanchard, M. Daturi, *Topics in Catalysis* 30–31 (2004) 31.
- [16] N. Macleod, R.M. Lambert, *Chemical Communications* 11 (2003) 1300.
- [17] N.W. Cant, M.J. Patterson, *Catalysis Letters* 85 (2003) 153.
- [18] Y. Ji, J.S. Choi, T.J. Toops, M. Crocker, M. Naseri, *Catalysis Today* 136 (2008) 146.
- [19] J. Szanyi, J.H. Kwak, D.H. Kim, S.D. Burton, C.H.F. Peden, *Journal of Physical Chemistry B* 109 (2005) 27.
- [20] J.M. Coronado, J.A. Anderson, *Journal of Molecular Catalysis A: Chemical* 138 (1999) 83.
- [21] W.S. Epling, A. Yezerets, N.W. Currier, *Catalysis Letters* 110 (2006) 143.
- [22] W. Bogner, M. Kramer, B. Krutzsch, S. Pischinger, D. Voigtlander, G. Wenninger, F. Wirbeleit, M.S. Brogan, R.J. Brisley, D.E. Webster, *Applied Catalysis B: Environmental* 7 (1995) 153.
- [23] E. Fridell, H. Persson, B. Westerberg, L. Olsson, M. Skoglundh, *Catalysis Letters* 66 (2000) 71.
- [24] Y. Li, S. Roth, J. Dettling, T. Buetel, *Topics in Catalysis* 16–17 (2001) 139.
- [25] L. Olsson, B. Westerberg, H. Persson, E. Fridell, M. Skoglundh, B. Andersson, *Journal of Physical Chemistry B* 103 (1999) 10433.
- [26] J. Despres, M. Elsener, M. Koebel, O. Krocher, B. Schnyder, A. Wokaun, *Applied Catalysis B: Environmental* 50 (2004) 73.
- [27] S. Hodjati, K. Vaezzadeh, C. Petit, V. Pitchon, A. Kiennemann, *Catalysis Today* 59 (2000) 323.
- [28] S. Erklfeldt, E. Jobson, M. Larsson, *Topics in Catalysis* 16–17 (2001) 127.
- [29] N. Cant, M.J. Patterson, *Catalysis Today* 73 (2002) 271.
- [30] W. Epling, J. Parks, N. Currier, A. Yezerets, *Catalysis Today* 96 (2004) 21.
- [31] B. Westerberg, E. Fridell, *Journal of Molecular Catalysis A: Chemical* 165 (2001) 249.
- [32] L. Liotta, G. Pantaleo, A. Macaluso, G. DiCarlo, G. Deganello, *Applied Catalysis A: General* 245 (2003) 167.
- [33] J.A. Pihl, J.E. Parks II, C.S. Daw, T.W. Root, *SAE Technical Paper Series* 2006-01-3441.
- [34] L. Cumararatunge, S.S. Mulla, A. Yezerets, N.W. Currier, W.N. Delgass, F.H. Ribeiro, *Journal of Catalysis* 246 (2007) 29.
- [35] L. Limousy, H. Mahzoul, J.F. Brilhac, F. Garin, G. Maire, P. Gilot, *Applied Catalysis B: Environmental* 45 (2003) 169.
- [36] M. Radojevic, *Environmental Pollution* 102 (S1) (1998) 685.
- [37] A. Amberntsson, H. Persson, P. Engström, B. Kasemo, *Applied Catalysis B: Environmental* 31 (2001) 27.
- [38] W.S. Epling, G.C. Campbell, J.E. Parks, *Catalysis Letters* 90 (2003) 45.
- [39] A. Lindholm, N.W. Currier, E. Fridell, A. Yezerets, L. Olsson, *Applied Catalysis B: Environmental* 75 (2007) 78.